PREPARATION AND CHARACTERIZATION OF POROUS ADSORBENT FOR CHROMIUM (VI) REMOVAL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF BACHELOR OF TECHNOLOGY

IN

CHEMICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

BY

SOURAV PATEL
ROLL NO. 10600030

under the guidance of

DR. SUSMITA MISHRA

DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA

CERTIFICATE

This is to certify that the thesis entitled "PREPARATION AND CHARACTERIZATION OF POROUS ADSORBENT FOR CHROMIUM (VI) REMOVAL" being submitted by Sourav Patel as an academic project in Chemical Engineering from the Department of Chemical Engineering of National Institute of Technology(Deemed University), Rourkela is a record of bonafide work carried out by him under my guidance and supervision.

Date

Rourkela

Prof. Dr. Susmita Mishra

Department of chemical engineering

NIT Rourkela

ACKNOWLEDGEMENT

I wish to express my sincere thanks and gratitude to Prof Dr. Susmita Mishra(Project Guide) for suggesting me the topic and providing me the guidance, motivation and constructive criticism throughout the course of the project.

I also express my sincere gratitude to Prof. Dr. S. K. Agarwal (HOD), Prof. Dr. R. K. Singh and Prof. Dr. H.M. Jena (Project Coordinator), of Department of Chemical Engineering, National Institute of Technology, Rourkela, for their valuable guidance and timely suggestions during the entire duration of my project work, without which this work would not have been possible

I would like to express my gratitude to Mr. A. Mohanty and Mr. Rajendra Tirkey for his all time technical support in carrying out the experiments and also to PhD research student Mr. Ramakhrishna Gottipati and M. Tech student Miss T. Deepthi for helping me in carrying out the experiments.

I am also grateful to Department, Chemical Engineering for providing me the necessary opportunities for the completion of my project. I also thank other staff members of my department for their invaluable help and guidance.

Sourav Patel (10600030)

Date Dept. of Chemical Engg.

Place: Rourkela NIT Rourkela

ABSTRACT

Chromium (VI) compounds are widely used in industry such as electroplating, meal finishing, leather tanning, pigments, etc. In recent years ground water is the main source of domestic water supply. Chromate poisoning cause severe skin disorders allergic dermatitis, liver and kidney damage. Thus chromium causes great public concern. A wide range of separation process has been investigated for the removal of Chromium (VI) from water. Adsorption using activated carbons posed to be the efficient method for removal of Chromium ions from water.

To use carbon as an adsorbent requires activation or surface modification of carbon. Methods like thermal and chemical methods of activation are common, but some problems are associated with them. Electrochemical method as one of the method of surface modification of commercially available activated carbon is applied. The result is better adsorption of Chromium (VI) ions. The present thesis includes various adsorption techniques. A literature review of adsorption characteristics has been included. Our project work include fabrication of an experimental setup, surface modification (oxidation at anode) in 0.5 M KCl solution at various intensity of currents, and latter comparisons of BET surface area, porosity, FTIR analysis (for identification of changes in bonds after electrochemical oxidation) and adsorption in spectrophotometer.

Surface area, pore volume and pore size all decrease with increase in current intensity. A significant loss in porosity and decrease in pore diameter were observed and is due to blockage of pores by formation of functional groups (carboxylic acidic groups, hydroxyl groups, lactonic grops, phenolic group) and aggregation of humic substances. As the intensity of oxidation is increased by increasing the intensity of source current the amount of adsorption also increases. Also it is observed that if the intensity of current is increased from 0.1 Amp to 2.1 Amp, the amount of adsorption increases. But as the current approaches to 2.1 Amp the adsorption amount doesn't change significantly. Sample oxidized at 2.1 ampere was analyzed in FTIR. In the FTIR spectra it is revealed that in some ranges dip in transmittance was observed. Suitable reasons were found out. This process of activation can be suitably applied for activation of carbon.

Key words: chromium, adsorption, electrochemical oxidation, BET surface area and FTIR

CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Pollution load of the environment is increasing day by day due to global rise in pollution and our quest to lead comfortable life resulting in explosive growth of industries, mining operation, and increase usage of natural resources. Chromium (a metal) compounds are widely used in industries such as electroplating, meal finishing, leather tanning, pigments, etc. Chromate poisoning causes severe skin disorders such as allergic dermatitis and liver and kidney damage.

Chromium salts are almost exclusively in the Chromium +3 oxidation state or the Chromium +6 oxidation state. In the environment Chromium +3 is typically not a problem; its relative toxicity is low. In contrast, Chromium +6 compounds are toxic chemicals and genotoxic carcinogens.

Currently USPEA has set a maximum contaminant level (MCL) for Chromium at 0.1 ppm in drinking water [Yue et al., Journal of Hazardous Material, (2009)]. The increasing concern with Chromium pollution significantly motivates the investigation and development of new and improved materials to address the problems.

There are many types of process available for water filtration. A water filter removes impurities from water by means of a fine physical barrier, a chemical process or a biological process. Filters clean water to various extents for drinking water, aquariums and irrigation, swimming pools.

Filtrations include sieving, reverse osmosis, ion exchange and adsorption mechanism. For plant, water filters include screen filters, cloth filters and sand filters. For home filters include granular activated carbon fibers (GAC), micro porous ceramic filters and carbon black resin (CBR) and ultra filtration membrane. Revere osmosis is most common today (hyper filtration) but it has disadvantage of getting corroded by chlorine. It is not capable of removing hydrogen H2S and

volatile organic compound (VOCs).Even though RO removes bacteria and viruses, it is not relied upon. Membranes are also costly.

Activated carbon is used in gold purification, metal extraction, water purification, gas purification, sewage treatment, medicine, air filters in gas masks and filter masks, filters in compressed air and many other applications like metal finishing, purification of electroplating solutions.

Activation of carbon involves pyrolysis of the precursor in an inert environment followed by activation. Activation process in common includes physical and chemical method. The disadvantage of the chemical activation process is lower purity of activated carbon is produced and this method also causes environmental pollution. The disadvantage of physical activation is higher consumption of energy as a high working temperature is required.

The advantage of using electrochemical method of oxidation is that it increases the metal binding capacity and tensile strength [Rengel-Mendez et al.,Trans Ichem E,(2000)].other advantages include [Berenguera et al., Carbon (2009)]: (i) reagent is electron, which can be supplied by a direct current source and transportation is not required; (ii)process can be done in situ; (iii)the treatment can be interrupted immediately and can be operated at room temperature and atmospheric pressure; (iv) the reaction conditions can be very precisely selected; and (v) oxidation and reduction processes are more selective and can be easily controlled by varying electrode potential.

CHAPTER 2

LITERATURE REVIEW

2.1Activated carbon:

Activated carbon is a form of carbon that is processed to have high porosity and thus to have a very large surface area available for adsorption.

Activated carbons are sometimes called as active carbons due to their highly developed internal surface area and porosity, sometimes described as solid sponges. The large surface area results in a high capacity for adsorbing chemicals from gases and liquids. The most widely used commercial active carbons have a specific surface area of the order of 800-1500 m2/g, as determined typically by nitrogen gas adsorption. Difference in pore size affects the adsorption capacity for molecules of different shapes and sizes, and thus is one of the criteria by which carbons are selected for a specific application. Porosity is classified by IUPAC into three different groups of pore sizes. They are:

Micropores: width less than 2 nm

Mesopores: width between 2 and 50 nm

Macropores: width greater than 50 nm

Micropores don't help much in adsorption process because of its small sizes to accommodate large molecules. So, to widen them different activation process are there which are as follows.

2.2 Production:

Activated carbon is generally produced from carbonaceous materials like nutshells, peat, wood, lignite and coal. It can be produced by one of the following processes:

2.2.1 Physical activation: By the help of gas the precursor is developed into activated carbon. One or combination of the following process can be used

- *Carbonization*: carbon containing material is pyrolyzed at temperature in the range of 600-900 °C, i.e. heating of the material in absence of air (inert atmosphere with gases like argon or nitrogen)
- *Activation/Oxidation* carbonized material is the exposed to oxidizing atmospheres (oxygen, carbon dioxide, or steam) at temperatures above 250 °C

2.2.1 Chemical activation: First of all the raw material is impregnated with chemicals like solution of strong acid (phosphoric acid, sulphuric acid), strong base (potassium hydroxide, sodium hydroxide) or strong base (zinc chloride). The precursor is carbonized at lower temperatures (450-900 °C). It is thought that the carbonization / activation step proceeds simultaneously with the chemical activation. This procedure is not suitable as some traces salt or acid or base may be present in the end product. But then also chemical activation is preferred over physical activation because of lower temperature of operation and shorter period of activation.

2.2.3 Electrochemical activation: It includes the oxidation of carbon by passage of electricity. It is a process of electrolysis where cathode is copper plate and carbon fibers as anode (which is in contact with another copper plate) .On application of power anodic oxidation of carbon fibers takes place .it introduces the new functional groups, such as –COOH, and –OH, onto carbon surfaces to increase the adsorption capacity and rate of the adsorption in the liquid phase.

2.3 Classifications:

Classification is done based upon their surface characteristics, behavior and preparation methods.

2.3.1 Powdered activated carbon (PAC)

PAC is powdered activated carbon or fine granules whose size is less than 1.00 mm. Their average pore diameter is between 0.15 to 0.25 mm. PAC is not generally used because of their high head loss and its inherent problem of non reactivation.

2.3.2 Granular activated carbon (GAC)

GAC are larger than PAC. Diffusion of the adsorbate is thus an important factor. GAC is used for deodorization, water treatment and separation of components in a flow system. Extruded activated carbon (EAC)

2.3.3 Extruded activated carbon(EAC)

EAC are cylindrical shaped activated carbon with diameters ranging from 0.8 to 45 mm. Since they are of bigger size they have high mechanical strength. For this reason these are used for gas phase applications.

2.3.4 Impregnated carbons

These types are used for the adsorption of H_2S and mercaptans. Inorganic metals like aluminum, manganese, zinc iron, lithium and calcium are impregnated upon them.

2.3.5 Polymers coated carbon

It is a process of preparing biocompatible polymer to give a smooth and permeable coat without blocking the pores.

2.4 Characterization of activated carbon

2.4.1 Gas adsorption

It is one of the experimental methods (SAXS, SANS. Mercury porosimetry, SEM, STM thermoporometry, NMR methods and others) available for the surface and pore size distribution [Lowell et al., Kluwer Academic Publn, (2004)]. The amount of adsorbate adsorbed on a solid surface depend upon absolute temperature T, the pressure P, and the potential E between the vapors (adsorbate), the surface (adsorbent). Therefore at some equilibrium pressure and temperature the weight W of gas adsorbed on a unit weight of adsorbent is given by:

$$W = f(P, T, E) \tag{2.1}$$

At constant temperature:

$$W=f(P,E) \quad (2.2)$$

A plot of W versus P, at constant T, is referred as the sorption isotherm of a particular gas-solid interface.

2.4.1.1 Physical and chemical adsorption

Depending upon the strength of the interaction, all adsorption process can be divided into two categories: chemical (irreversible) and physical adsorption. Chemical adsorption is characterized mainly by large interaction potential, which leads to high heat of adsorption often approaching to chemical bonds. This fact, coupled with other spectroscopic, electron spin resonance and magnetic susceptibility measurements confirms that chemisorptions involve chemical bonding of adsorbate (gas or vapor) with the interface. It is also associated with activation energy [Lowell et al., Kluwer Academic Publn, (2004)]. Molecules that are chemical adsorbed are more localized than physical adsorption. Physical adsorption (or reversible) makes it suitable for surface adsorption by the following way:

1. Physical adsorption is accompanied by low heat of adsorption.
2. In physical adsorption more than one layer of molecules can be adsorbed
3. Equilibrium reached is fast, as activation energy is not required.
4. Adsorbed molecules are restricted to sites.
5. Pores can be filled completely.

2.4.1.2 Physical adsorption force

Adsorption of gas leads to decrease in entropy. Condensed state is more ordered than gaseous state. To have spontaneity of adsorption process Gibbs free energy, ΔG should be negative. Assuming entropy change is not much and enthalpy change, ΔH always negative, makes ΔG always negative [Lowell et al., Kluwer Academic Publn, (2004)].

$$\Delta H=\Delta G+T\Delta S \quad 2.3$$

Vander wall force of attraction is responsible for physical adsorption

1. Dispersion forces are present regardless of the nature of other interactions and are responsible for major part of the adsorptive-adsorbate potential.
2. Ion-dipole: present in an ionic solid and a polar adsorbate

3. Ion-induced dipole: preset between an polar solid and polarizable molecule
4. Dipole-dipole: a polar solid and polarizable molecule
5. Quadruple interactions: interactions among symmetrical molecules, such as nitrogen and carbon dioxide have this kind of interactions

2.4.1.3 Physical adsorption on macropores (assumed as a planar molecule)

The London-vander wall's interaction energy Us(z) of a gas molecule with a planar surface is given by[Lowell et al., Kluwer Academic Publn, (2004)]:

$Us(z)=C_1z^{-9}-C_2z^{-3}$

Where C_1 and C_2 are constants and z is the distance between gas molecules from the surface. The first term express repulsive force while second term express fluid wall interactions. The attractive interaction energy at the minimum relative close distance is ten times greater than the thermal energy (K_bT)](Rouquerol et al)

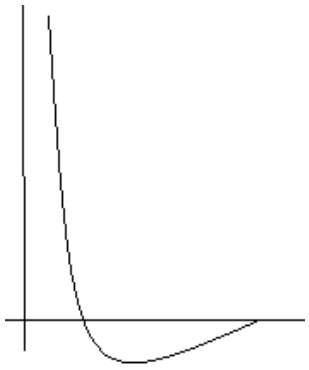


Fig 2.1: schematic illustration of adsorption potential ε on planar surface [Rouquerol et al., Academic Press, (2009)]

2.4.1.4 Physical adsorption on mesopores

Adsorption behavior depends upon the fluid wall interaction as well as attractive interactions between fluid molecules.

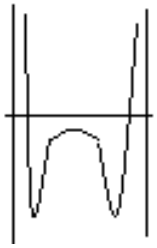


Fig 2.2 schematic illustration of adsorption potential ε on mesopores [Rouquerol et al., Academic Press, (2009)]

2.4.1.5 Physical adsorption on micropores

As the pores are very small the interactions is dominant by fluid-wall interactions

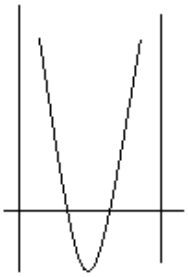


Fig 2.3: schematic illustration of adsorption potential ε on micropore [Rouquerol et al., Aademic Press, (2009)]

2.4.2 Isotherms

Adsorption isotherm is the amount of adsorbate adsorbed on the adsorbent as a function of its pressure (gas) or concentration (liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials.

Different adsorption isotherms models are as follows:

2.4.2.1 Freundlich Isotherms

The first mathematical fit to any isotherm was published by Freundlich and Küster in 1894. It is purely an empirical formula for gaseous adsorbate.

$$\frac{x}{m}=kP^{1/n} \quad (2.5)$$

Where, x is the quantity of adsorbate adsorbed, P is the pressure of adsorbate, m is the mass of the adsorbent and k and n are empirical constants for each adsorbate-adsorbent pair at a given temperature. The function reaches to an asymptotic maximum as pressure increases.

2.4.2.1 Langmuir theory

The problem encountered in Freundlich isotherm is that the calculated surface area will be less than the actual surface area. It is because, molecules (adsorbate) adheres tightly to the surface without allowing rearrangement of themselves [Lowell et al., Kluwer Academic Publn, (2004)]

Langmuir adsorption isotherm was based on monolayer physical adsorption. It is based upon four assumptions:

1. The surface of the adsorbent is uniform, i.e. all the adsorption sites are equivalent.
2. All adsorption occurs through the same mechanism.
3. Adsorbed molecules do not interact with each other.
4. At the maximum adsorption, only a monolayer is formed, molecules of adsorbate do not deposit on other adsorbed molecules of adsorbate.

According to kinetic theory number of molecules striking unit are of surface per second

$$N = \frac{\bar{N}P}{\sqrt{2\pi\bar{M}oRT}} \qquad (2.6)$$

Where

$\bar{N}$=avagadro's no.

P is absolute Pressure

$\bar{M}$= molecular weight

R = gas constant

T= absolute temperature

If θo is the fraction of the surface unoccupied then number of collisions with bare surface per unit area per second is

$\frac{dN}{Dt}$=kpθ (2.7)

$where\ k = \frac{\bar{N}}{\sqrt{2\bar{M}RT}}$ (2.8)

The no of molecules striking and adhering to each unit area of surface is

$$N_{ads} = kP\theta oA_1 \quad (2.9)$$

The rate at which adsorbed molecules leave

$$N_{des} = N_m\theta_1 v_1 e^{-E/RT} \quad (2.9)$$

Where, N_m is the number of molecules in a completed monolayer of unit area. At equilibrium

$$N_m\theta_1 v_1 e^{-E/RT} = kP\theta oA_1 \quad (2.10)$$

As $\Theta o = 1-\theta_1$ then

$$N_m\theta_1 v_1 e^{-E/RT} = kPA_1 - \theta_1 kPA_1 \quad (2.11)$$

Solving

$$\theta 1 = \frac{kPA1}{\mathrm{Nmv1e^{-E/RT}+kPA1}} \quad (2.12)$$

Allowing

$$K = \frac{kA1}{Nmv1} \mathrm{e^{-E/RT}} \quad (2.13)$$

Substituting K in Θ_1

$$\theta_{1=} kP/(1+ KP) \quad (2.14)$$

Assuming one layer coverage we can write,

$$\theta 1 = \frac{N}{Nm} = \frac{W}{Wm} \quad (2.15)$$

Where, N is incomplete monolayer. W/Wm is the weight adsorbed relative to the weight adsorbed in a completed monolayer

$$\frac{W}{Wm} = \frac{KP}{1+KP} \quad (2.16)$$

$$\frac{P}{W} = \frac{1}{KWm} + \frac{P}{Wm} \qquad (2.17)$$

2.4.2.3 Brunauer, Emmett and Teller (BET) Theory

BET theory is an extension of Langmuir monolayer adsorption theory.

It is an extension of the Langmuir theory. BET theory is a theory for monolayer molecular adsorption to multilayer adsorption with the following hypotheses: 1.Gas molecules physically adsorb on a solid surface infinitely. Adsorption takes place in layers. 2. There is no interaction among each adsorption layer. 3. The Langmuir theory can be applied to each layer. BET equation is expressed by (2.19):

$$\frac{1}{v\left[\left(\frac{Po}{P}\right)-1\right]} = \frac{c-1}{vmc1}\left(\frac{P}{Po}\right) + 1 \qquad (2.19)$$

Where, P and P_0 are the equilibrium and the saturation pressure of adsorbate at the given temperature of adsorption, v is the adsorbed gas, v_m is the monolayer adsorbed gas quantity and c is the BET constant, which is expressed by :

$$c = \exp\left(\frac{E1-EL}{RT}\right) \qquad (2.20)$$

E_1 is the heat of adsorption for the first layer; E_L is the heat of adsorption for the second and higher layers and is equal to the heat of liquefaction.

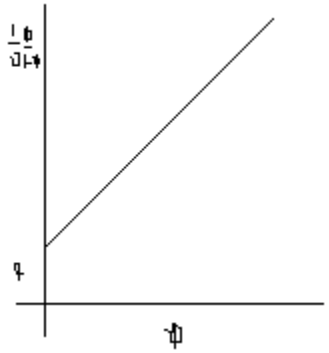


Fig 2.4: BET plot

Equation (2.19) is an adsorption isotherm and when plotted a straight line is got with $1 / v[(P_0 / P) - 1]$ on the y-axis and $\varphi = (P/P_0)$ on the x-axis. The linear relationship of this equation is

maintained only in the range of $0.05 < P / P_0 < 0.35$. The slope is a and intercept is I and this line can be used to calculate the monolayer adsorbed gas quantity Vm and the BET constant c. The following equations can be used:

$Vm=(1/(a+I))$ where N is avagadro,s number (2.21)

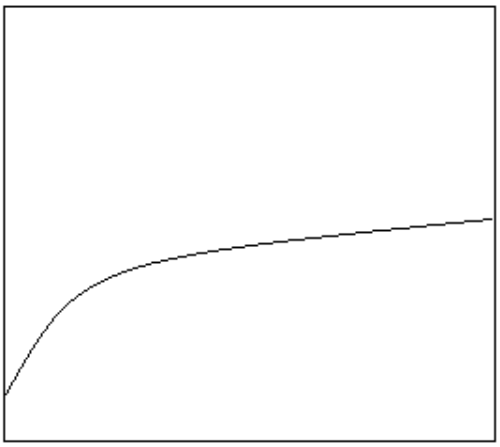
V is the molar volume of gaseous adsorbent

a is the molecular weight of adsorbate

2.4.3 Classification of adsorption isotherm

Based on extensive literature survey, performed by Brunauer, Demming, Demming and Teller, the IUPAC published a classification of six adsorption isotherm [Sing et al., Pure Applied Chem. (1985)]:

Type I: the curve is concave to P/Po axis and the amount adsorbed reaches to a limiting value as P/Po→1. It indicates adsorption to a few molecular layers. Chemical adsorption often shows this kind of isotherm. If physical adsorption is taking place then adsorption on micropores layer takes place.

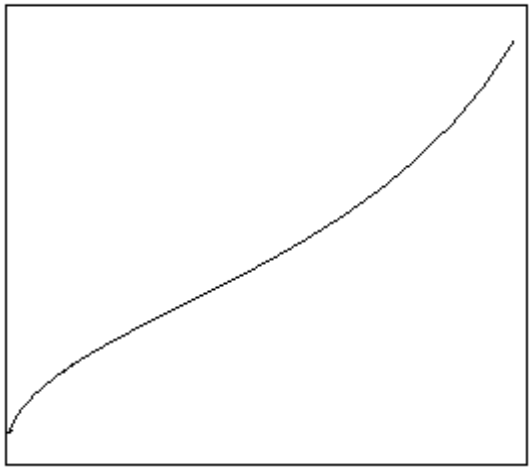


Amount adsorbed

P/Po

Fig 2.5: Sorption isotherm (Type 1) [Sing et al., Pure Applied Chem. (1985)]:

TypeII: First unrestricted monolayer adsorption takes place and then multilayer adsorption takes place. After inflection point molecular force of attraction is more than adsorbate-adsorbent force of attraction.

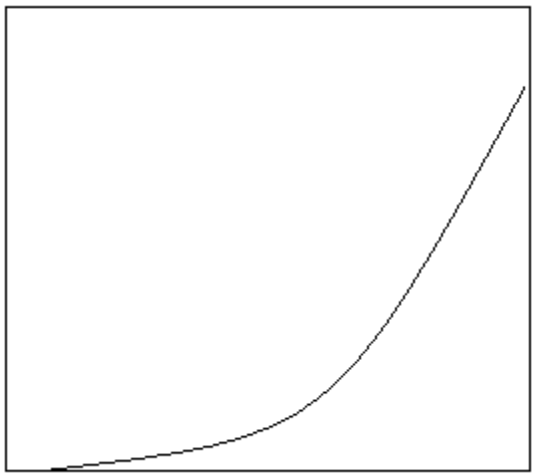


Amount adsorbed

P/Po

Fig 2.6: Sorption isotherm (Type II) [Sing et al., Pure Applied Chem. (1985)]:

Type III: adsorbate-adsorbate force of attraction is predominant over adsorbate-adsorbent force of attraction.



Amount adsorbed

P/Po

Fig 2.7: Sorption isotherm (Type III) [Sing et al., Pure Applied Chem (1985)]:

Type IV: this indicates mesopores structures.

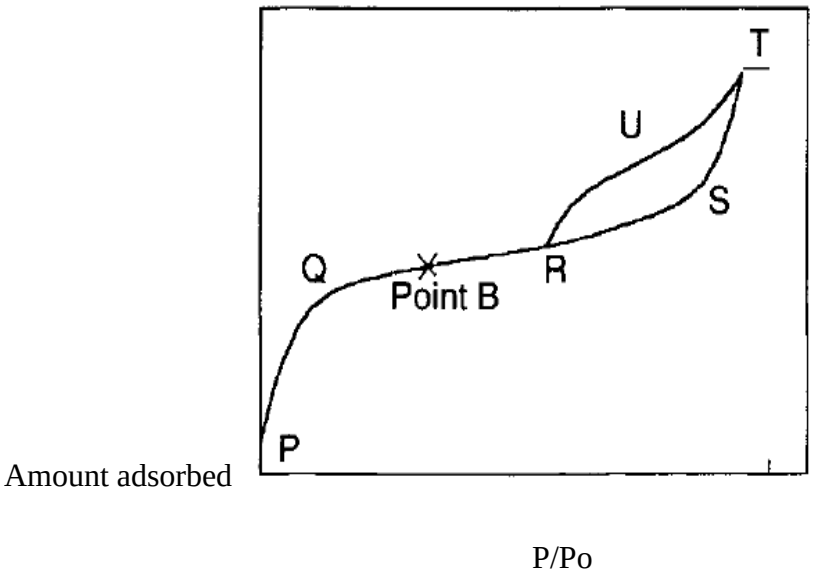
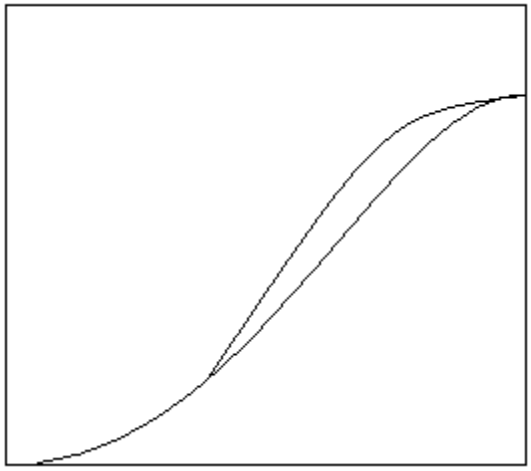


Fig 2.8: Sorption isotherm (Type IV) . [Marsh and Rodriguez-Reinoso et al., Activated Carbon, Elsevier publn. (2006)]

According to Marsh et al. the line PQ describes adsorption in the microporosity. The smaller is the micropore size, the steeper will be the line PQ. The line QR shows continuity of adsorption in the smallest mesopores. RS indicates progressive feeling of the mesopores concluding the largest of the mesopores is at position S. On decreasing the pressure of the nitrogen in the equipment, the equilibrium positions (desorption isotherm), do not follow the line SR but the line SUR to create hysteresis loop meeting at point R. This indicates desorption line equilibria follows a curved meniscus of desorption. If the line RS is vertical then it indicates mesopores are of equal sizes. If the value of P/Po is 0.90 then it correspond to pore size of 10 nm. Similarly for P/Po= 0.95 then pore size is of 20 nm, and P/Po= .995 indicates pore sizes is of 200 nm.

Type V: It shows pore condensation and hysteresis. Initial part shows weak attractive interactions between the adsorbent and the adsorbate.



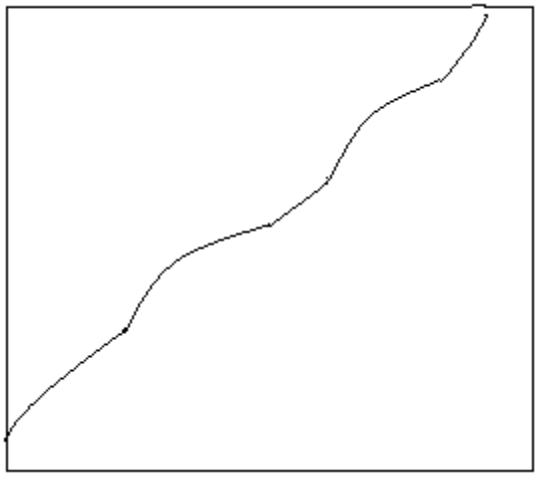
Amount adsorbed

P/Po

Fig 2. 9 Sorption isotherm (Type V) [Sing et al., Pure Applied Chem (1985)]

Type VI:

It represent stepwise multilayer adsorption on a uniform, non-porous surface [Hill T. L, Journal phys. Chem.,(1955)] particularly by spherically symmetrical, non polar adsorptive. The sharpness of steps depends upon on the homogeneity of the adsorbent surface, the adsorptive and the temperature.



Amount adsorbed

P/Po

Fig 2.10: Sorption isotherm (Type VI) [Sing et al., Pure Applied Chem (1985)]

2.5 Spectrophotometer

It is an instrument to measure the adsorbance or transmittance through a solution. Light that passes through the solution is detected by a photo tube that converts it into electric signal.

The scale is usually calibrated in two ways: percent transmittance, which scales from 0 to 100; and absorbance, which scales from 0 to 2. The amount of light absorbed is proportional to the concentration of a compound. Beer's Law explains the relationship between absorbance at a given wavelength and concentration.

a= ebc

Where a=absorbance

e = molar extinction coefficient

b = distance/ path followed

c = concentration of the solution

The relationship between absorbance and concentration is linear and the concentration increases as the absorbance increases.

2.6 Quantachrome BET surface area analyzer

BET surface area analyzer is based upon the theory of BET theory of adsorption of gas molecules on the surface of the adsorbent. A multilayer may form before all the monolayer adsorption takes place. Total monolayer capacity is then determined from BET equation without any influence of multilayer. It has a degasser to free any volatile material or impurity. Then surface area analysis is done.

2.7 FTIR analyzer

Infrared (IR) spectroscopy measures the infrared intensity versus wavelength (wave number) of light.

It detects the vibration characteristics of the functional groups present in a sample irrespective of the structure of material. When an infrared light interacts with the sample, chemical bonds stretch, contract and bend. As a result, the functional groups tend to adsorb infrared radiation in a specific wave number.

2.7.1 Spectra of transmittance with different wave numbers

The spectra of different functional groups are as follows:

Alkanes

- -C–H- 3000–2850 cm^{-1}
- =C–H 1000-650 cm^{-1}
- -C=C- 1690-1650 cm^{-1}
- =C–H 3110-3010 cm^{-1}

Alkynes

- –C≡C–H: C–H 3330-3270 cm^{-1}
- –C≡C–H: C–H 700-610 cm^{-1}
- –C≡C– 2260-2100 cm^{-1}

Alkyl Halides

- C–Cl 850-550 cm^{-1}
- C–Br 690-515 cm^{-1}

Aromatics

- Aromatic hydrocarbons stretch 1600-1585 cm^{-1} and 1500-1400 cm^{-1}

Ketones

-C=O stretch:

- aliphatic Ketones 1715 cm^{-1}
- α, β-unsaturated Ketones 1685-1666 cm^{-1}

Aldehydes

- H–C=O 2830-2695 cm^{-1}
- -C=O stretch:

- aliphatic aldehydes 1740-1720 cm^{-1}
- α,β -unsaturated aldehydes 1710-1685 cm^{-1}

Alcohols

- O–H 3500-3200 cm^{-1}
- C–O 1260-1050 cm^{-1}

Carboxylic acids

- O–H 3300-2500 cm^{-1}
- -COOH 3300-2500 cm^{-1}
- C=O 1760-1690 cm^{-1}

Esters

- C=O stretch
  - aliphatic 1750-1735 cm^{-1}
  - α, β-unsaturated 1730-1715 cm^{-1}
- C–O stretch 1300-1000 cm^{-1}

Amines

- N–H 3400-3250 cm^{-1}
  - primary amine: two bands in 3400-3300 and 3330-3260 cm^{-1}
  - secondary amine: one band in 3350-3310 cm^{-1}
  - tertiary amine: this region don't have any band
- ≡C-N= stretch (aromatic amines) 1335-1250 cm^{-1}
- =N–H bend (primary amines) 1650-1580 cm^{-1}
- ≡C–N= stretch (aliphatic amines) 1250–1020 cm^{-1}

2.8 Previous work

On application of positive potential on carbon, anodic oxidation of carbon fibers takes place. It introduces new functional groups, such as –COOH, and –OH, onto the carbon surfaces to

increase the adsorption capacity and rate of the adsorption in the liquid phase. Generally it increases the adhesive property and strength.

Carbon fibers were subjected to electrochemical oxidation (25 ^{o}C, 0-450 mAmp, NaOH as electrolytic solution) and then dried (110 C for 6 hr). Nitrogen adsorption isotherms for BET surface area and pore volumes were measured at 77K [Park et al., Carbon (1999)].

Result [Park et al., Carbon (1999)] shows specific surface area, average pore diameter, micropore volume does not change a much. Surface acidity of ACFs was determined by titration with hydrochloric acid. There was a significant increase in acidity. Result also shows that the amount of adsorption and the adsorption rate of Chromium from the aqueous solution increase with increase electrochemical oxidation of ACF.

GACs (170-210 μM) were washed and dried (at 378 K) until no change in weight was noticed. It was then electrochemically oxidized at 3mAmp/m^2 (range 0.01 to 3mAmpm^{-2}) for 3 hrs in an electrolyte solution (0.5 M. Conc.) at 293-295 K. Surface area, acidic sites, batch and continuous sorption experiment and kinetics were analyzed [Rengel-Mendez et al., Trans IchemE, (2000)].

Result [Rengel-Mendez et al., Trans IchemE, (2000)] shows BET surface area decreases, total oxygen containing functional groups increased by 3.36 times. This increased sorption capacity by 16.5 times. Cadmium uptake increased as PH increased (4-6).adsorption rate also increased[4]. Kinetic experiment shows that the adsorption rate for cadmium was rapid and 96% of fractional approach to equilibrium was attained in 12 minutes using both unoxidized electrochemical oxidized carbon.

The pitch based (bundle type) were washed with deionized water, then dried(24 hrs, 80 ^{o}C), and then subjected to electrochemical oxidation in the aqueous solution of 10 wt wt% H_3PO_4 and NH_4OH, whereby negative ions were attracted to the surface (7 A , 10 min). It was then washed and dried (6 hr, 110 ^{o}C) [Park et al., Mat Sc and Engg. (2005)].

Result [Park et al., Mat Sc and Engg. (2005)] shows total pore volume and micropore volume decreases. This is due to increase in oxygen containing functional groups and blockage of the pores. BET surface area decreased. Adsorption isotherm (% change in concentration vs. time) of

Cr (VI), Cu (II), and Ni (II) from 0-180 minutes shows that the initial adsorption rate of Cr (VI) ion on the ACFs increases rapidly, especially due to molecular sieve structure of the ACFs Also the amount of Chromium (VI) adsorbed is comparatively much larger than the amount of Copper (II) and Nickel (II) adsorbed under similar conditions. This can be imagined due to high ionic radius of copper (II) 0.70 A^o and Nickel (II) 0.69 A^o compared to that of Chromium (VI) 0.52 A^o, induces a quick saturation of adsorption sites because of steric crowding.

CHAPTER 3

METHODS & EXPERIMENTAL PROCEDURES

This chapter describes materials used, fabrication and outlines the experimental procedure.

3.1 Chemicals used

Pure and analytical grade chemicals were used in all experiments. Potassium dichromate and 1,5-Diphenylcarbazide was procured from Merck, Chemical, India. Fresh stock solution for Cr (VI) solution was prepared following standard procedure. Others chemical used are sulphuric acid (reagent used during absorbance analyses in spectrophotometer), acetone (for washing) and potassium chloride (for preparation of electrolytic solution). Besides that distilled water is used for washing.

3.2 Sample used

The carbon that is taken for electrochemical oxidation for surface modification is commercially available chemically activated carbon under the brand name Kalpaka chemicals "KALBON GAQ Water Treatment". The granular activated carbon is used for water treatment applications. It is used for removal of taste, colour, odour and dissolved organic contaminants from potable and process water. It is also used in DM plant filters, Tap water filters, Desalination plants and Aquariums.

Specifications:

Size 12x40 ASTM, oversize 0.6%, undersize 0.3%
Iodine No. 1050 mgram/gm
Hardness 98.60%
Moisture 2.677%

Ash 2.15%

3.3 Glassware and Apparatus used

All glass wares (Conical flasks, Measuring cylinders, Beakers, Petri plates and Test tubes etc.) used are of Borosil/Rankem. The instruments and apparatus used throughout the experiment are listed below:

Table 3.1: List of Instruments used during the whole experiment their make and function

Instruments	**Make**	**Function**
Electronic weight balance	Sartorius	To measure weight
PH meter	EuTech Instruments	Measurement of pH
Spectrophotometer(UV/Vis)	Jasco(V-530)	absorbance
Shaker	Environmental Orbital Shaker	To stir the content
Surface area, porosimetry	Quantachrome autosorb-1	Measurement of surface area, porosity
Oven	Shivaki	To dry the samples
ampere meter	UNI-T Dt 380 D	multimeter

3.4 Fabrication

To perform the electrochemical oxidation process of commercially activated carbon following materials are required for fabrication

1. Perplex column (I. D. 2.75”)
2. Plastic net
3. Anode copper plate(4”x4”x1.968”)
4. Plastic stands
5. GI sheet
6. Epoxy Adhesive (araldite)
7. Liquid gasket sealant (Autobond)
8. Transformer (A.C. to D.C.)
9. D.C. Gear motor
10. Cathode copper plate (2”x12”)

Fig 3.1: photograph of plastic net, perplex column, 5 mm copper plate, plastic stand used

Fig 3.2: photograph of G.I. sheets, gasket sealant and epoxy adhesive

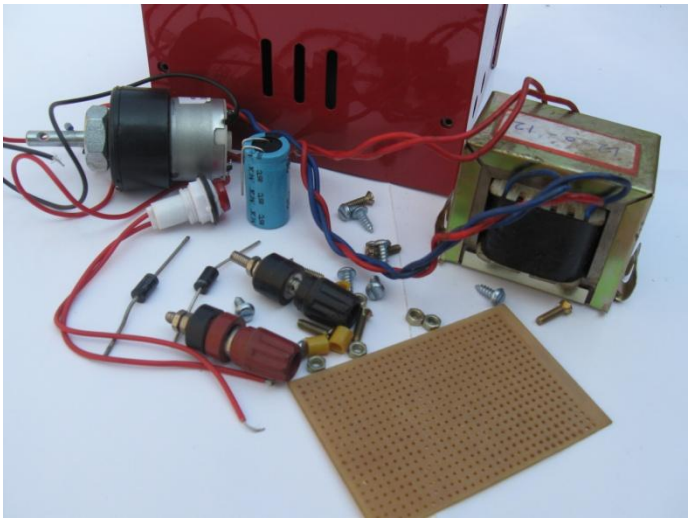


Fig 3.3: photograph of gear motor and power supply

3.4.1 Fabrication of anode copper plate

To cut the anode side of copper plate which is 50 mm thick requires an electrically operated hex saw. The metal plate was fitted into bench vice. This work was carried out in the workshop department. With a glass marking pen the plate was marked so that it just fits into the perplex column. The plate was cut near to a circular shape. The instruments used area shown below.

To bring it into perfect circular shape the edges were polished in a grinder.

Fig 3.4: anode copper plate

Table 3.2: List of mechanical Instruments used during fabrication

Mechanical instruments	**Make**	**Function**
hex saw	Bosch	To cut metals
Cutter	Bosch	To cut metal plates
Bench vice	------	To hold the metal
Filling machine	------	To file the edges

3.4.2 Fabrication of perplex column

From a large perplex column (1.5’ x 2 .75” I.D.) two equal length (20 mm) of perplex column were cut manually in the fluid flow lab.

First a plastic net is wrapped around Perspex column. It is tightly tied on another side. This net is then glued with one side (edges) of the column with the help of epoxy adhesive. To another column liquid gasket sealant is applied on its edges. These were then dried for 2 days. Extra net was cut. Three legs were glued to the column at a uniform height. Finally an arrangement as shown in figure is got.

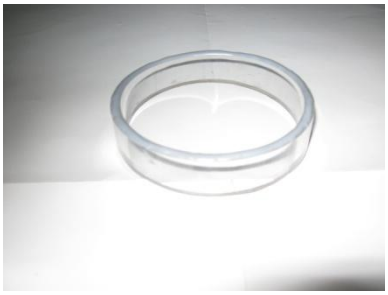


Fig 3.5: perplex column

3.4.3 Fabrication of stand (support to the perplex columns)

Three equal size plastic stands (3mm x 20 mm x 55 mm) were cut from a large cuboidal plastic fiber in the fluid flow lab manually with a help of a hex saw.

3.4.4 Fabrication of clamps (to hold the columns)

To hold the perplex column tightly clamps were required. No clamps were available in the market as required. So from G.I. plates clamps were made manually. G.I. sheets were cut of dimensions 7mm x 60mm. These were later bend by an angle of 90^{o} at both sides. The edges were also bent by 90^{o} so that it doesn't slips out from the column. The screws were drilled at one end to have screws in them.

Fig 3.6: clamps

3.4.5 Fabrication of stirrer

The stirrer was powered by 12 V D.C. supply. Motor was held by a stand. It was dipped into the water bath (not in the electrolyte). This was used if sufficient rise in temperature was detected

3.5 Experimental setup

Setup consists of a plastic tub of 5000 ml capacity. Inside it, there is a cathode plate, stirrer, thermometer and an arrangement for oxidation of activated carbon. This arrangement consists of a three legged perplex column of 2 cm height (diameter 2.75'') with a net covering the whole area inside it. Above it is a filter paper that rests on the net. This holds the chemically activated carbon. To restrict the flow of electrolytic solution from sideway another perplex column (2 cm height x 2.75''dia) with a gasket sealant is kept over it. To have a tight fitting between these two perplex column three clamps (made GI sheet) is used. This has screws to alter the degree of tightening. This allows solution to come to the activated carbon through filter paper. A circular copper plate of 5 mm thickness, just fitting into the perplex column act as anode. Thick copper plate is taken to restrict electrolytic solution to come to top of it and inhibit oxidation there.

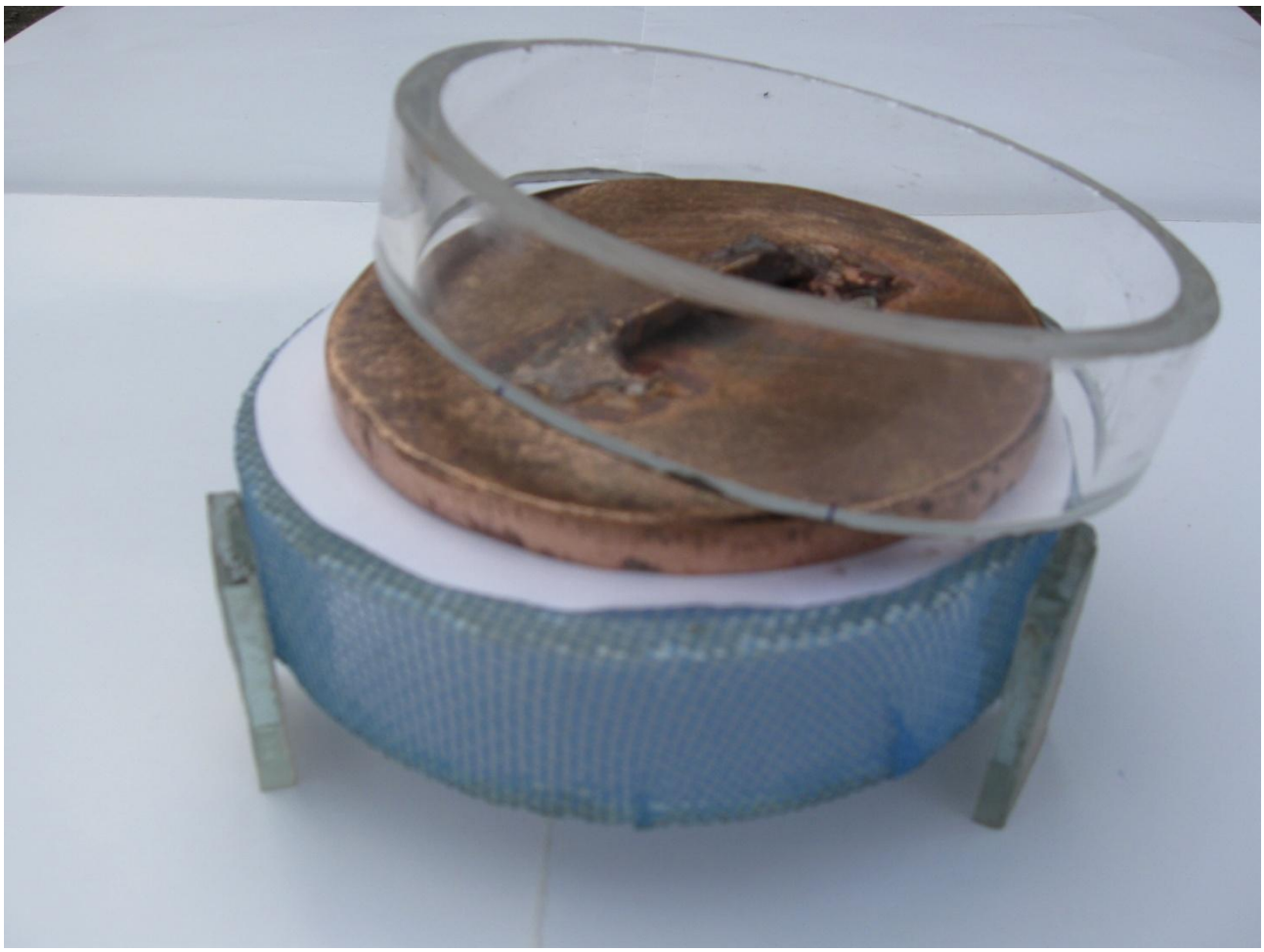


Fig: 3.7: setup for oxidation of carbon

The top anode is connected to positive potential of power supply. This can give current ranging from 0 Amp to 4.5 Amp. The cathode is connected to negative potential of power supply. In between these is an electronic multi meter. It measures the applied current. If high current is applied, temperature rise may be encountered. So an arrangement of stirrer is done. This is there to stir the water bath and maintain a uniform temperature throughout the oxidation process.

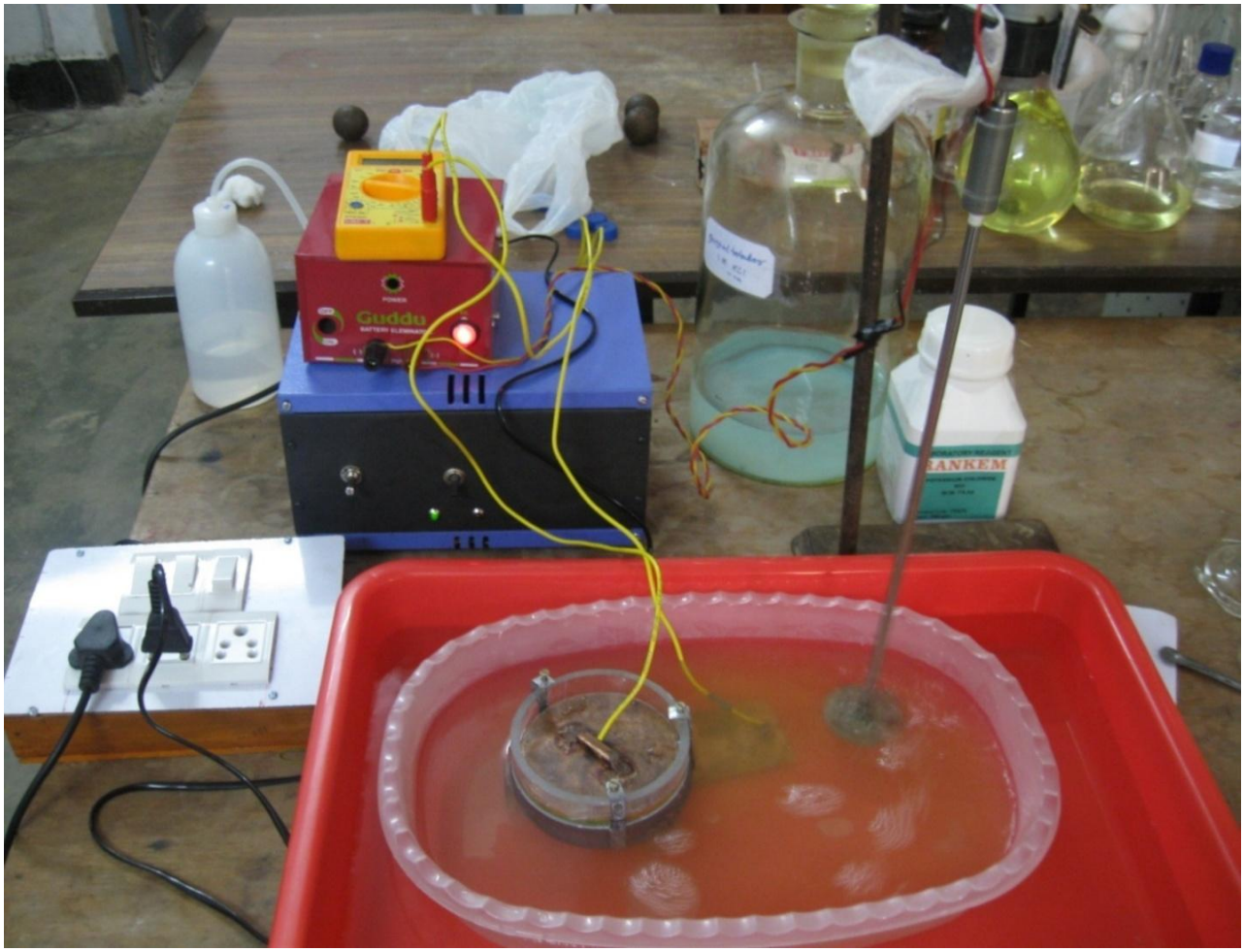


Fig 3.8: experimental setup

3.6 Preparation of adsorbent

In between the two columns a filter paper was kept. It is then held tight by the help of clamps. It has screws to tighten them. Now 10 grams of the sample (carbon) is taken and spread over the filter paper. Filter paper doesn't allow granular carbon to move into solutions. Electrolyte

was then added so that it just immerses the sample. Above the sample the anode was placed. Below it cathode plate was placed.

3.6.1 Preparation of electrolytic solution

The solution is of potassium chloride. 0.5% M KCl solution is prepared. At a time 2 liters of solution were required. So in 2 liters of distilled water 74.56 grams of KCl salt was added.

3.6.2 Oxidation of activated carbon

Before start of oxidation the sample was allowed to wet with the solution for 20 minutes. Then oxidation of sample was done for 20 minutes. Current intensity was adjusted by the variac (of the power supply). After oxidation the sample was taken in a beaker and washed continuously in distilled water for 20 minutes.

3.6.3 Drying of oxidized (surface modified sample)

The sample was dried in oven at $85^{o}C$ for 24 hours.

3.7 Method for surface area and porosity analyses

Sample of known weight (approx. 0.100 gm) is taken in the glass tube of degasser. Degassing is done (for 2 to 3 hours, depends upon the sample) at $250^{o}C$. It helps in removal of any adsorbed gas etc. from the sample. After that it is fitted into the quantachrome analyzer (dipped in liquid nitrogen) to analyze BET surface area and porosity.

3.8 Method of absorbance analyses in spectrophotometer

3.8.1 Preparation of potassium dichromate solution

28.23 milligrams of $K_2CR_2O_7$ salt was taken in 1 liter of distilled water to prepare standard solution of 10 milligrams of chromium solution in 1 liter of water.

3.8.2 Preparation of standard indicator

The indicator for absorbance analyses is prepared by adding 250 milligrams of 1,5 diphenylcarbazide in 50 ml of acetone. It should be always freshly prepared. If Indicator is kept open in light, it undergoes photo reaction. So it should be always kept in a dark bottle.

3.8.3 Adsorbance of chromium

At first 2 mg/L, 4 mg/L, 6mg/L, 8mg/L and 10 mg/L was adsorbed on the carbon (1 gram) at a PH 5. 2 mg/L was made by adding 20 ml of 10 mg/L of Cr solution and 80 ml of distilled water (total solution is then 100 ml). The activated sample was proportionally taken as 100 milligram. Similarly 2 mg/L, 4 mg/L, 6mg/L, 8mg/L and 10 mg/L was made. They were then shacked and allowed to adsorb for 2 hours. Their adsorption on carbon was analyzed in spectrophotometer. Then all the 6 samples (0.1 Amp. 0.5 Amp, 0.9 Amp, 1.3 Amp, 1.7 Amp and 2.1 Amp) were analyzed in similar manner.

3.8.4 Method for spectrophotometeric analysis

1 ml of sample was taken in a cleaned testube. To it 9 ml of distilled water was added. So dilution factor is 10. To it 1 drop concentrated sulphuric acid and 1 ml of indicator was added. This was then well shacked. A purple color comes. In the spectrophotometer both the analyzer was kept initially with distilled water. In the sample side, sample was taken. Absorbance was then studied for each sample.

3.9 Method for FTIR analysis

The oxidized activated carbon sample (at 2.1 Amp) was analyzed in FTIR. This was done to know the changes in functional groups that took place during the course of oxidation.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Absorbance analyses

To know the optimum current that has to be supplied to oxidize the commercially available activated carbon, absorbance of adsorbed chromium solution was analyzed for five different concentration (2 mg/L, 4 mg/L, 6mg/L, 8mg/L and 10 mg/L). After 2 hours absorbance were analyzed in spectrophotometer. The table shows the absorbance of different samples at different current of oxidation. A standard calibration curve y=0.00058 x- 0.0091 is taken from R. Gottipati and S. Mishra (2010), where y is absorbance in spectrophotometer and x is concentration of chromium in solution.

Concentration of chromium after 2hours of adsorption in 100 milligram of prepared adsorbent (0.1 Amp. 0.5 Amp, 0.9 Amp, 1.3 Amp, 1.7 Amp and 2.1 Amp) shacked at 200 rpm at a pH of 5 and at N.T.P. with different initial concentration of chromium solution (2 mg/L, 4 mg/L, 6mg/L, 8mg/L and 10 mg/L) at different current of oxidation

Table 4.1: concentration of chromium at different intensity of oxidation

Current(amps)→ Concentration(mg/L)↓	**0.1**	**0.5**	**0.9**	**1.3**	**1.7**	**2.1**
2	8.1123	7.2361	6.0126	5.3571	4.3812	3.5984
4	6.8191	5.1097	3.9891	3.2657	2.8916	2.2019
6	4.8514	3.4513	2.8006	2.6364	2.2561	1.9122
8	3.1233	2.2101	1.8107	1.6398	1.7961	0.6846
10	1.5157	1.3918	0.8113	0.7795	0.7810	0.6243

A graph is plotted of this absorbance with X axis as concentration of the adsorbed sample of different initial concentration with Y axis showing the current.

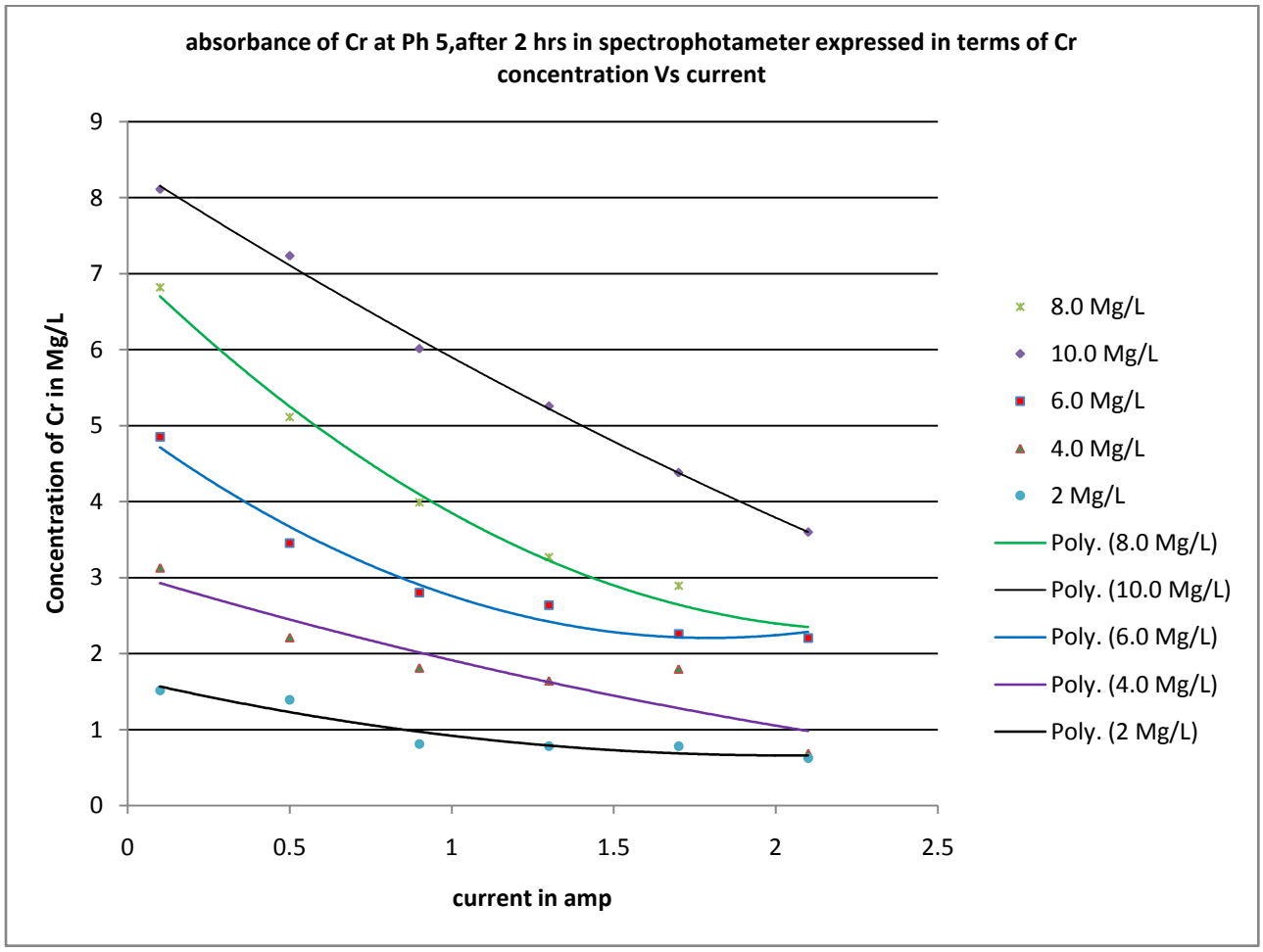


Fig 4.1: effect of absorbance with different concentrations of Chromium solutions and current.

From the graph, it is concluded that as the intensity of current is increased from 0.1 Amp to 2.1 Amp, the amount of adsorption increases. But as the current approaches to 2.1 Amp the adsorption amount doesn't change significantly. So the concentration of chromium in solution does not change. According Yue et al. the adsorption capacity increases as electrochemical oxidation increases but to some extent [Yue et al., Carbon (1999)]. If it is considered that, 2.1 Amp as the final optimum current of oxidation then we can study adsorption characteristics and FTIR analysis of the sample oxidized at 2.1 Amp.

While for raw unoxidized adsorbent could only reduce the concentration of 2 mg/L, 4 mg/L, 6mg/L, 8mg/L and 10 mg/L to 1.6129 mg/L, 3.3527 mg/L , 5.1036 mg/L, 6.9810 mg/L and 8.6819 mg/L respectively.

4.2 FTIR analysis

Infrared (IR) spectroscopy is a technique which measures the infrared intensity versus wavelength (wave number) of light. It detects the vibration characteristics of chemical functional groups present in the sample. The sample oxidized at 2.1 Amp for 20 minutes in 0.5 M KCl solution was sent to Metallurgy and Materials Engg. Department for analysis. A single FTIR report is of 60 pages and cannot be accommodated in this thesis. A short FTIR report containing 22 values is given below:

Table 4.2: FTIR spectra Report for oxidized carbon at 2.1 Amp

Wave numbers λ (Cm-1)	Transmittance (%)
798.529824	27.439363
952.835104	26.318827
1107.140834	25.598868
1261.945664	24.978838
1415.750944	24.771823
1570.056274	23.469321
1724.361504	24.364813
1878.666784	23.831731
2032.972064	23.487372
2189.777344	23.214774
2341.582624	20.602263
2495.887904	22.830144
2650.193184	22.736291
2804.498464	22.591292
2598.803744	22.634076
3113.109024	22.211814
3267.414304	22.149373
3421.71984	22.340114

3518.160384	22.395942
3730.330144	21.587001
3884.635424	20.995117
4000.304384	21.714227

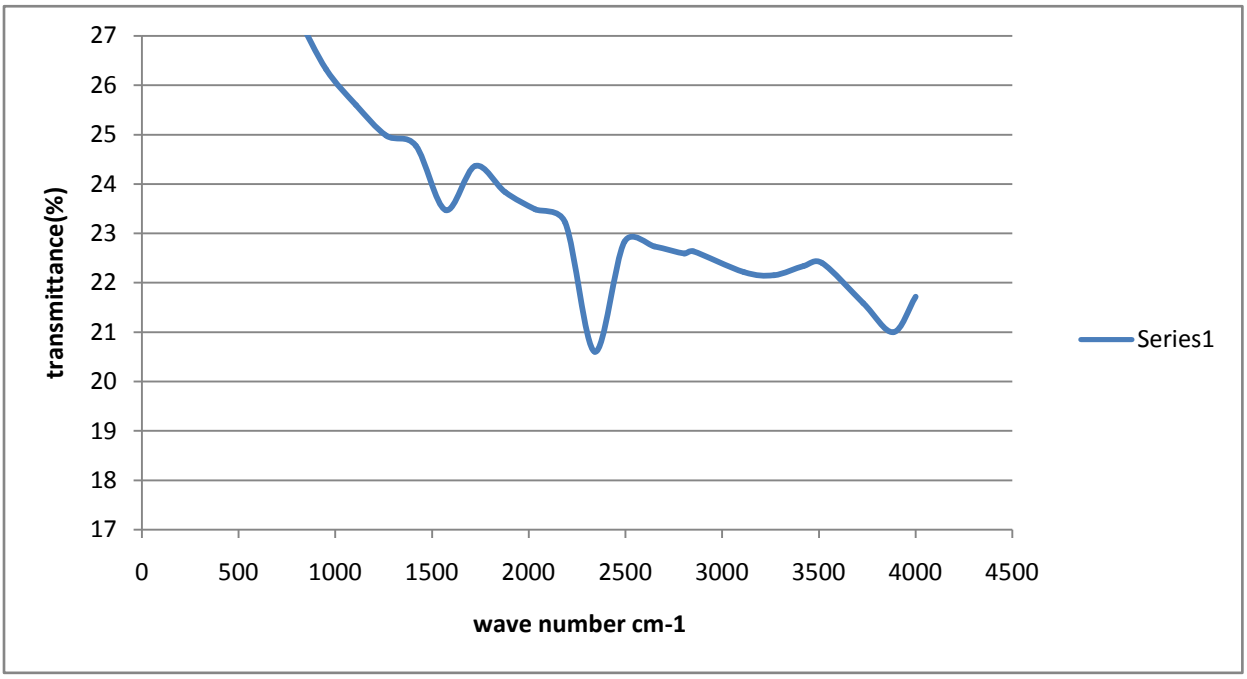


Fig 4.2: FTIR spectra of ACF of 2.1 Amp oxidized carbon

Table 4.3: FTIR report of raw sample with 22 chosen points

Wave number λ (Cm-1)	Transmittance (%)
4000.36	0.425
3676.32	0.406
3514.3	0.416
3352.28	0.424
3190.26	0.426
3028.24	0.424
2866.22	0.429
2704.2	0.421
2542.23	0.419
2380.15	0.432
2218.138	0.413
2056.11	0.409
1732.07	0.385
1570.05	0.394

1408.03	0.391
1083.99	0.398
921.97	0.385
840.96	0.379
759.95	0.372
678.94	0.347
597.93	0.359
516.92	0.3478

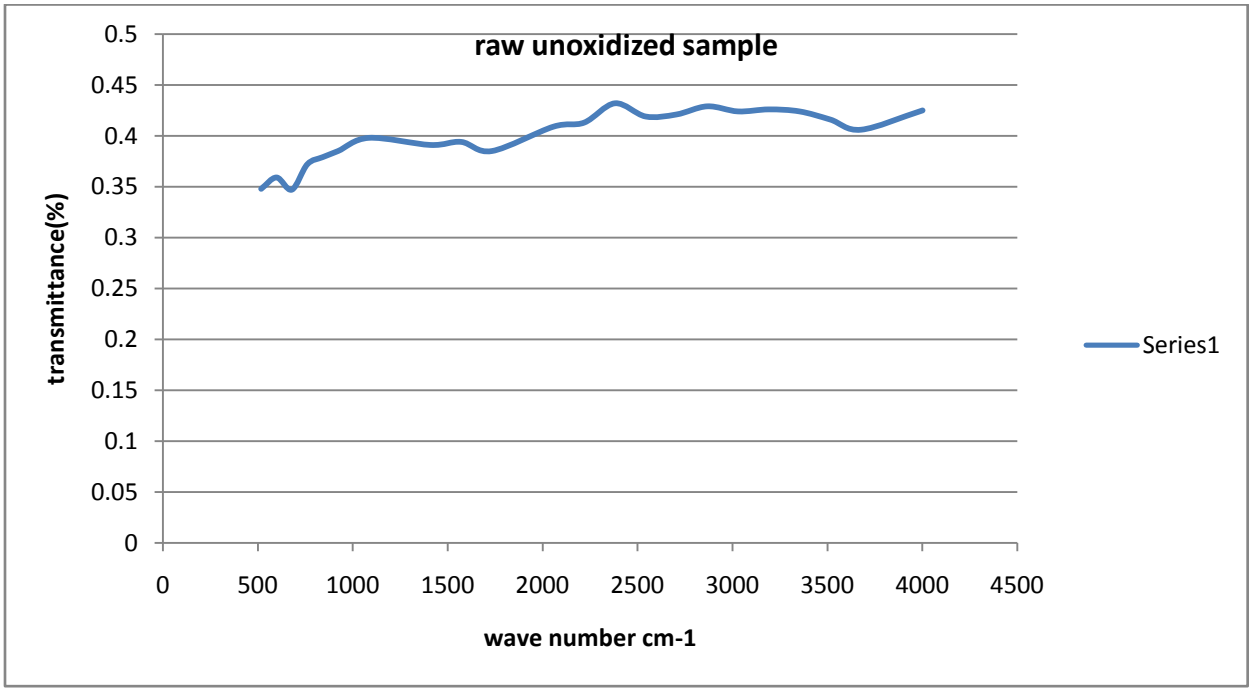


Fig 4.3: FTIR spectra of unoxidized sample

In the FTIR spectra it is revealed that in the range of 3700-3400 cm-1 a dip in transmittance was observed. It is because of stretching of O-H vibrations. Similarly a dip in transmittance was observed in 2460-2100 cm-1. It reveals of the presence of -C≡C- groups. The adsorption bands in 1640-1500 cm-1 region is because of the overlapping of aromatic ring bands and double bands(C=C) vibrations with the bands of C=O moieties. It is also supported by [Park et al., Carbon (1999)].

4.3 Surface area and porosity

BET surface area was analyzed in quantachrome autosorb-1. The table below shows the analysis of raw sample (unoxidized) and oxidized samples. P/Po is the ratio of pressure of N2 over carbon to that of atmospheric pressure. At first adsorption is done and then desorption is done.

Table 4.4: pressure ratio P/Po to that of amount adsorbed or desorbed (unoxidized, oxidized with 0.1 Amp, 0.5 Amp, 0.9 Amp)

0.0 amp		0.1 amp		0.5 amp		0.9 amp	
P/Po	Vol. of N2 adsorbed	P/Po	Vol. of N2 adsorbed	P/Po	Vol. of N2 adsorbed	P/Po	Vol. of N2 adsorbed
0.057706	417.5714	0.10435	322.3492	0.10822	333.3722	0.099761	325.8922
0.14925	435.8996	0.19825	329.3567	0.19909	340.6309	0.20592	335.1825
0.25553	443.663	0.30637	333.3975	0.30581	345.0577	0.30583	339.4699
0.35794	448.5536	0.39797	335.7343	0.39699	347.6258	0.4103	342.8379
0.45939	452.1429	0.49927	337.8634	0.49918	349.799	0.49983	344.9
0.5811	455.2634	0.60164	339.5076	0.60078	351.7206	0.59999	346.8369
0.65912	457.9755	0.7027	340.9611	0.70178	353.3371	0.69837	348.932
0.75934	460.7411	0.8024	342.4297	0.80057	355.1557	0.79979	350.8107
0.85623	464.3192	0.8996	344.2372	0.90077	357.0505	0.89934	352.8495
0.95774	467.7098	0.9994	347.6717	0.9994	361.1433	0.9994	357.6185
P/Po	Vol. of N2 adsorbed	P/Po	Vol. of N2 adsorbed	P/Po	Vol. of N2 adsorbed	P/Po	Vol. of N2 adsorbed
0.94342	468.4286	0.89917	345.4867	0.89869	358.9196	0.90295	354.3932
0.83707	467.4241	0.79324	344.7903	0.79407	358.0629	0.79254	353.5981
0.73769	466.433	0.69282	344.0711	0.69333	357.1907	0.69348	352.6427
0.63861	464.9107	0.5931	343.2704	0.59411	356.1732	0.5943	351.5427
0.53862	463.1138	0.50107	341.4023	0.49916	354.3567	0.50094	349.5495
0.44832	456.6563	0.39176	337.4326	0.3926	349.4825	0.3922	344.7728
0.34063	452.5982	0.30035	335.2087	0.30072	347	0.30164	342.2349
0.24174	448.1317	0.19245	331.3757	0.19301	342.7464	0.19341	337.8117
0.14545	441.3103	0.099886	324.5872	0.1002	335.2949	0.10235	330.2621

Table 4.5: pressure ratio P/Po to that of amount adsorbed or desorbed (unoxidized, oxidized with 1.3 Amp, 1.7 Amp, 2.1 Amp)

1.3 amp		1.7 amp		2.1 amp	
P/ Po	Vol. of N2 adsorbed	P/Po	Vol. of N2 adsorbed	P/Po	Vol. of N2 adsorbed
0.10848	325.3566	0.11034	300.3299	0.098841	295.6516
0.19751	332.8717	0.20541	307.0896	0.20659	304.0231
0.30606	337.4637	0.29697	310.6519	0.30569	307.702
0.39721	340.0687	0.39999	313.4545	0.39656	309.9966
0.49868	342.4263	0.5017	315.8013	0.49682	312.1418
0.60089	344.3363	0.60456	317.6065	0.60095	313.7839
0.70166	346.1101	0.70448	319.187	0.70136	315.2118
0.79962	347.9738	0.80463	320.7701	0.80178	316.6311
0.90044	350.003	0.9055	322.4182	0.90102	318.2041
0.9994	354.8768	0.9994	327.8013	0.9994	322.281
P/Po	Vol. of N2 adsorbed	P/Po	Vol. of N2 adsorbed	P/Po	Vol. of N2 adsorbed
0.90022	351.9121	0.90057	324.0922	0.90136	319.7148
0.79399	350.9111	0.79191	323.2208	0.79412	318.912
0.6936	349.9515	0.69133	322.3909	0.69339	318.1315
0.59413	348.8566	0.59193	321.4156	0.59418	317.2186
0.50109	346.8081	0.49557	319.7506	0.50006	315.5841
0.39177	341.9626	0.4024	315.9338	0.39202	311.7071
0.30068	339.4636	0.2978	313.3351	0.30116	309.5517
0.19311	335.1122	0.20097	309.8922	0.19338	305.7156
0.10162	327.4646	0.097002	302.4974	0.10229	299.0359

4.4 Adsorption isotherm

Adsorption isotherms of the samples were plotted.

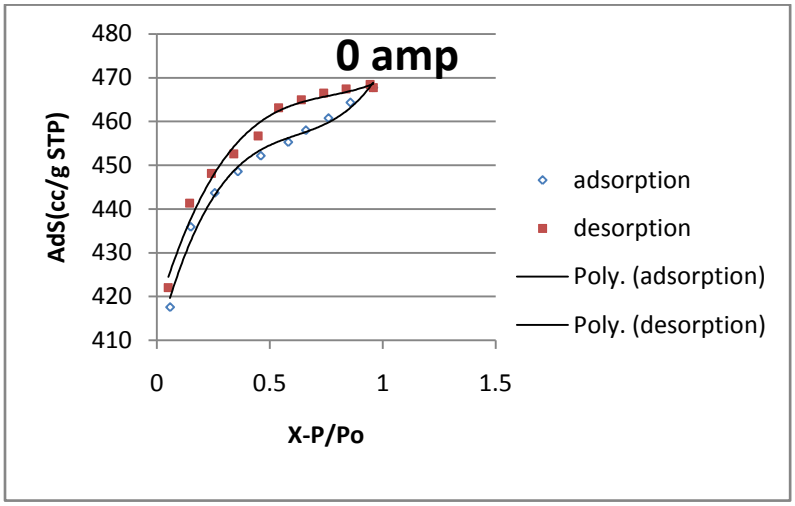


Fig 4.4: adsorption desorption isotherm of raw sample

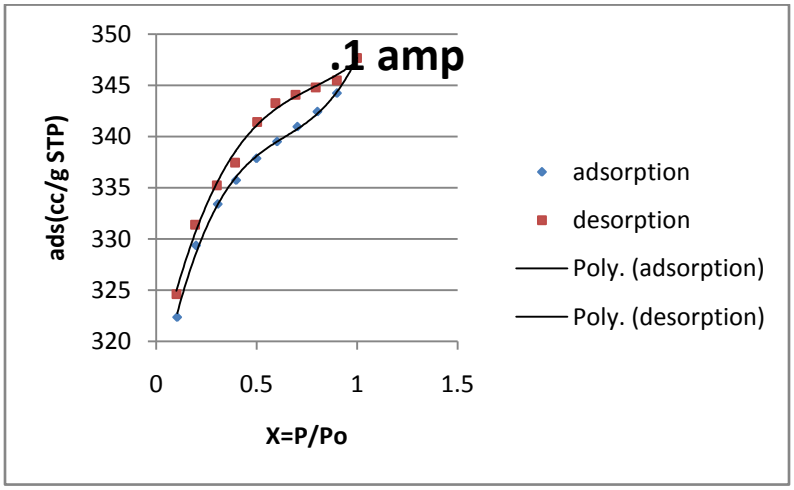


Fig 4.5: adsorption desorption isotherm of 0.1 Amp

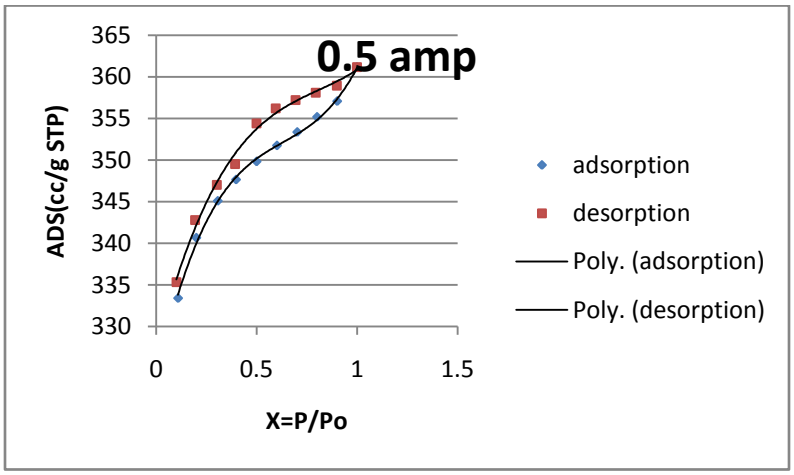


Fig 4.6: adsorption desorption isotherm of 0.5 Amp

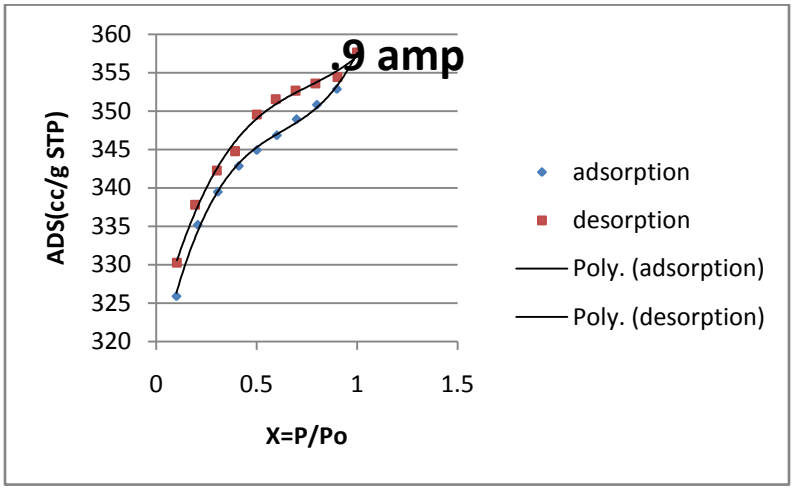


Fig 4.7: adsorption desorption isotherm of 0.9 Amp

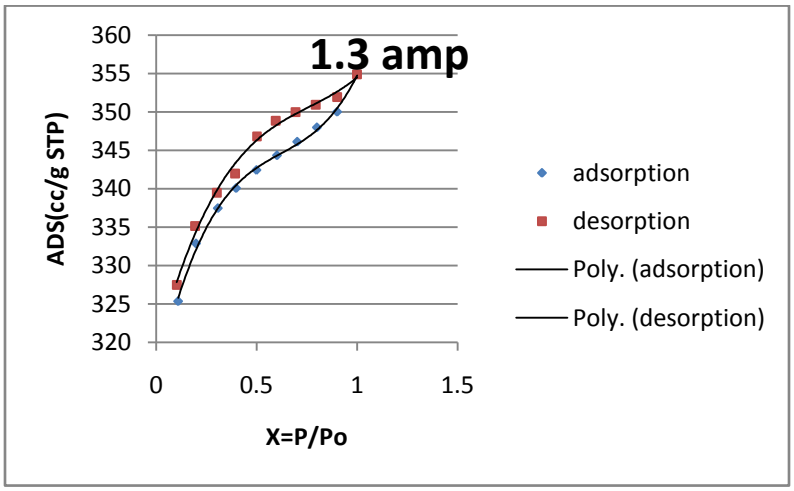


Fig 4.8: adsorption desorption isotherm of 1.3 Amp

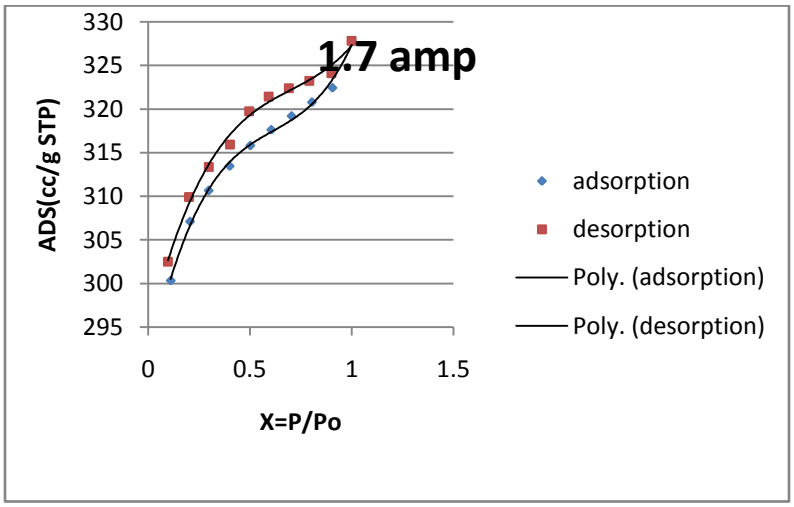


Fig 4.9: adsorption desorption isotherm of 1.7 Amp

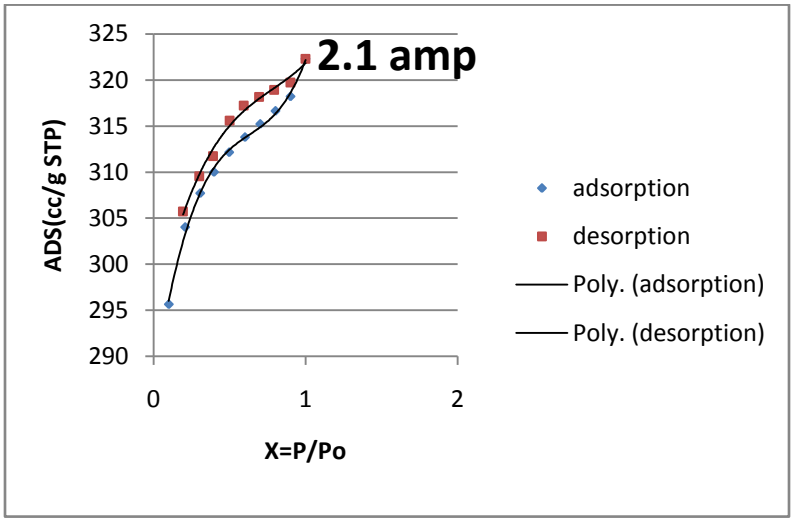


Fig 4.10: adsorption desorption isotherm of 2.1 Amp

All these isotherm best fit to the Langmuir isotherm. According to IUPAC it is best suited to Type IV. These isotherms show that the activated carbon is typically for mesoporous materials. Its hysteresis loop is the characteristic to Type IV of isotherm

4.5 Analysis of surface area with current

The quatochrome autosorb-1 directly gives the surface area of the samples.

Table 4.6: Current and surface area relationship

Current Amp	Surface area (m2/gram)
0	1216
0.1	991.33
0.5	972.66
0.9	967.31
1.3	950.36
1.7	887.24
2.1	887.69

These values were plotted in Microsoft Exel and following graph was got

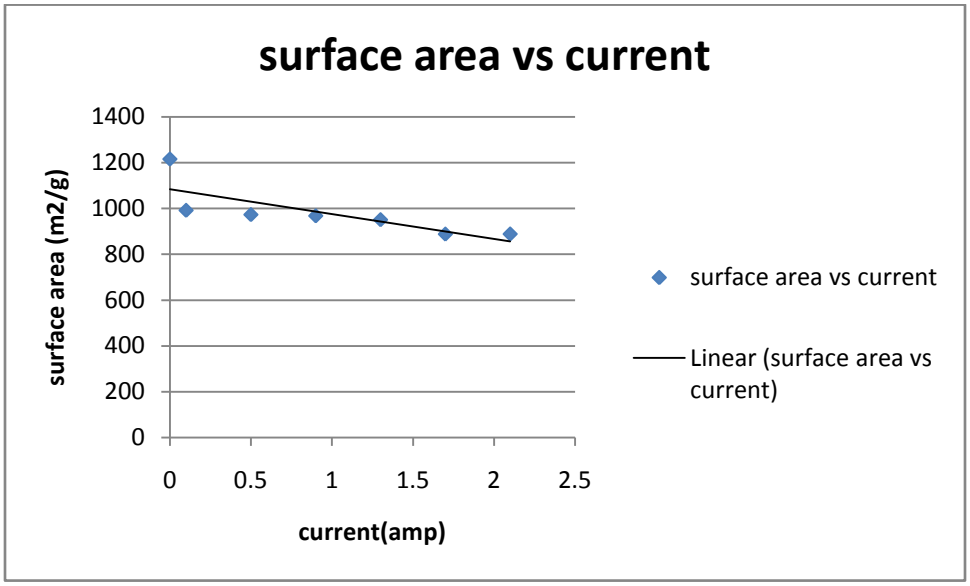


Fig 4.11: Affect of intensity of oxidation on Surface area

Decrease in surface area is resulted from pore blockage by formation of functional groups. This crowds the entrance of the pores. The oxidation process also causes the destruction of pore [Park et al., Mat Sc and Engg. (2005)]. But this doesn't have any negative affect on adsorption of chromium ions.

4.6 Analysis of pore volume with current

The pore volume of different oxidized sample including that of raw sample is given below. The result show that, as the intensity of oxidation is increased the pore volume decreases.

Table 4.7: Current and pore volume relationship

Current amp	Pore volume (cm 3/gram)
0	0.1625
0.1	0.07013
0.5	0.07602
0.9	0.08683
1.3	0.08006
1.7	0.07285
2.1	0.07425

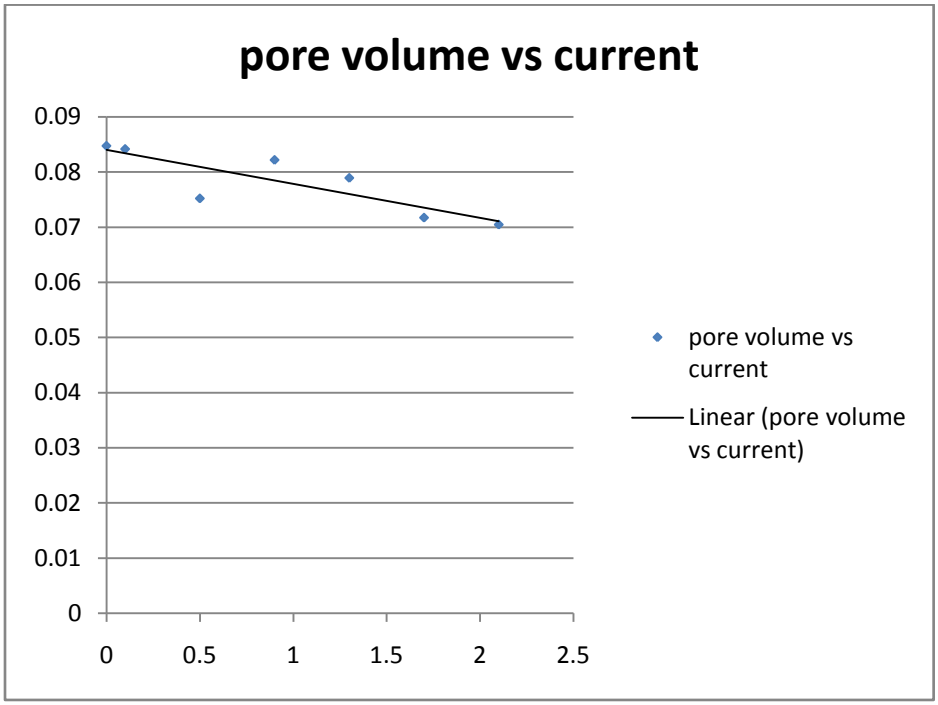


Fig 4.12: Affect of intensity of oxidation on pore volume

This satisfies the decreases in specific surface area. As surface area decreases the pore volume must decrease. A significant loss in porosity were observed and attributed to blockage of pores through formation of functional groups (carboxylic acidic groups, hydroxyl groups, lactonic grops, phenolic group) and humic substances [Park et al., Mat Sc and Engg. (2005)].

4.7 Analysis of pore diameter with current

The presence of micropores is not easily determined. Their contribution to adsorption is less.

Table 4.8: Current and pore size relationship

Current (amp)	Pore size (diameter in A^o)
0	86.05
0.1	18.19
0.5	18.31
0.9	18.27
1.3	18.28
1.7	18.52
2.1	18.26

There is a large contribution of mesopores and macropores. The pore diameter which is measured by analyzer is mainly due to contribution of mesopores and macropores. The pore diameter of samples before and after oxidation is given below.

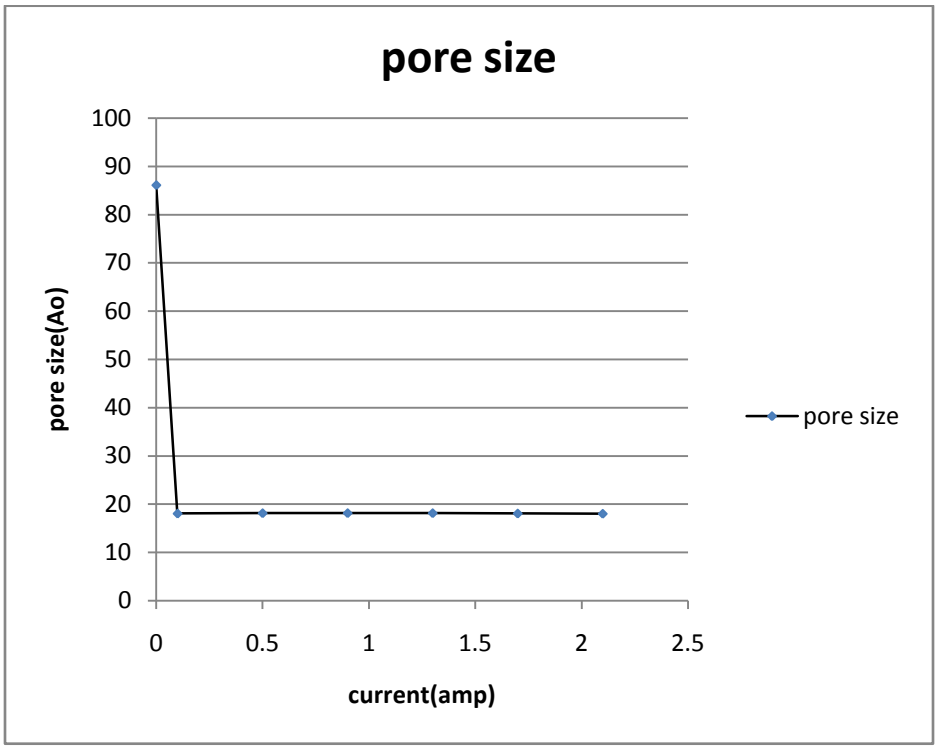


Fig 4.13: Affect of intensity of oxidation on pore size

Decrease in pore volume support decrease in pore size. Strict decrease in pore size may be attributed due to presence of some amount of humic substances in micro & mesopores. Humic substances are generated during the course of experiment. These are some salts of metals like copper and potassium that are used during the course of experiment.

CHAPTER 5

CONCLUSIONS

The electrochemical method of activation (surface modification) of commercially available activated carbon was studied.

1. Fabrication of setup was done. Fabrication was done in a manner to have large surface area available for carbon to undergo oxidation.

The parameters on which adsorption study was done include the affect of current on surface area, pore volume and pore size. Then optimum current for oxidation was found out. Sample oxidized at optimum current was analyzed in FTIR to know the reasons

2. Surface area, pore volume and pore size all decrease with increase in current intensity. Decrease in surface area is resulted from pore blockage by formation of functional groups. The oxidation process also causes the destruction of pore resulting in final decrease in surface area.
3. A significant loss in porosity were observed and is due to blockage of pores by formation of functional groups (carboxylic acidic groups, hydroxyl groups, lactonic grops, phenolic group) and aggregation of humic substances.
4. Decrease in pore volume support decrease in pore size. Strict decrease in pore size may be attributed due to presence of some amount of humic substances in micro & mesopore. Humic substances are generated during the course of experiment. These are some salts of copper and potassium that are generated during the course of experiment.
5. As the intensity of oxidation is increased by increasing the intensity of source current the amount of adsorption also increases. This concludes that degree of formation of functional groups (that are responsible for adsorption) increases with increase in current.
6. Also it is concluded that as the intensity of current is increased from 0.1 Amp to 2.1 Amp, the amount of adsorption increases. But as the current approaches to 2.1 Amp the adsorption

amount doesn't change significantly. Therefore the optimum current for oxidation is 2.1 Ampere.

7. Sample oxidized at 2.1 ampere was analyzed in FTIR. In the FTIR spectra it is revealed that in the range of 3600-3200 cm-1 a dip in transmittance was observed. It is because of stretching of O-H vibrations. Similarly a dip in transmittance was observed in 2500-2300 cm-1. It reveals of the presence of -C≡C- groups. The adsorption bands in 1640-1500 cm-1 region suggests the overlapping of aromatic ring bands and double bands (C=C) vibrations with the bands of C=O moieties.

In our project we could reduce the concentration of chromium by 3.5 times. Adsorption capability is much greater than the carbon activated bye other mode of activation. Conclusion is that it will be a better mode of activation of carbon.

CHAPTER 6

REFERENCES

Berenguer R., Marco-Lozar J.P., Quijada C., Cazorla-Amoro´s D., Morallo´n E., Effect of electrochemical treatments on the surface chemistry of activated carbon. Carbon (2009).

Hill T. L. Corresponding states in multilayer step adsorption., *J*ournal of *Physics and. Chemistr*. (*1955).*

Lowell S., Shields J. E., Thomas A. M., Thommes M., Characterization of porous solids and powders. Kluwer academic Publishers (2004).

Park S.J., Kim Y. M., Adsorption behaviors of heavy metal ions onto electrochemically oxidized activated carbon fibers. (2005).

Park S.J., Park B.J., Ryu S. K., Electrochemical treatment on activated carbon fibers for increasing the amount and rate of Cr(VI) adsorption. (1999).

Rangel-Mendez J., Tai M. H., Streat M.Removal of cdmium using electrochemically oxidized activated carbon. Trans IChemE (2000).

Rouquerol F., Rouquerol J., Sing K., Adsorption by powders and porous solids. Academic Press (1999).

Sing K.S.W., Everret D.H., Haul R. A., Moscou L, Pierotti R. A., Rouqueral J., Siemieniewska T. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure and Applied Chemistry (1985).

Yue Z., Bender S. E., Wang j., Economy J., Removal of Cr (VI) by Low cost chemically activated carbon materials from water. Journal of Hazardous material. (2009).

Yue Z. R., Jiang W., Wang L., Toghiani H., Gardner S. D., Pitman Jr., Adsorption of precious metal ions onto electrochemically oxidized carbon fibers. Carbon (1999).